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Wong et al.

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[54] **SYNDIOTACTIC 1,2-POLYBUTADIENE SYNTHESIS**

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[57] **ABSTRACT**

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Syndiotactic 1,2-polybutadiene is a thermoplastic resin which has double bonds attached in an alternating fashion to its polymeric backbone. Films, fibers and molded articles can be made utilizing syndiotactic 1,2-polybutadiene. It can also be blended into rubbers and cocured therewith. In such applications, sometimes it is beneficial for the syndiotactic 1,2-polybutadiene to have more than one melting point. This invention discloses a process for preparing syndiotactic 1,2-polybutadiene having at least two different melting points which comprises: polymerizing 1,3-butadiene monomer in an aqueous medium in the presence of (1) a catalyst composition which is made by reacting (a) at least one cobalt compound selected from the group consisting of (i) β -diketone complexes of cobalt, (ii) β -keto acid ester complexes of cobalt, (iii) cobalt salts of organic carboxylic acids having 6 to 15 carbon atoms and (iv) complexes of halogenated cobalt compounds of the formula CoX_n , wherein X represents a halogen atom and n represents 2 or 3, with an organic compound selected from the group consisting of tertiary amine alcohols, tertiary phosphines, ketones and N,N-dialkylamides, (b) at least one organoaluminum compound of the formula AlR_3 , wherein R represents a hydrocarbon radical of 1 to 6 carbon atoms and (c) at least one conjugated diene; (2) at least one member selected from the group consisting of carbon disulfide, phenyl isothiocyanate and xanthic acid; and (3) at least one melting-point regulator and (4) a sodium halide salt or a potassium halide salt.

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[52] **U.S. Cl.** **526/123.1; 526/94; 526/140; 526/141; 526/340.1**

[58] **Field of Search** 525/88; 526/94, 526/123.1, 140, 141, 142, 169.1, 185, 340.1

[56] **References Cited**

U.S. PATENT DOCUMENTS

3,778,424	12/1973	Shotaro Sugiura et al.	260/94.3
3,901,868	8/1975	Ueno et al.	260/94.3
4,153,767	5/1979	Ueno et al.	526/141
4,394,473	7/1983	Winter et al.	524/226
4,429,085	1/1984	Henderson et al.	526/92
4,751,275	6/1988	Witte et al.	526/139
4,790,365	12/1988	Sandstrom et al.	152/510
4,902,741	2/1990	Burroway et al.	524/836
4,957,970	9/1990	Holsapple et al.	525/99
5,011,896	4/1991	Bell et al.	526/92
5,021,381	6/1991	Burroway et al.	502/117
5,405,816	4/1995	Burroway	502/108
5,468,822	11/1995	Tsumimoto et al.	526/340.1

FOREIGN PATENT DOCUMENTS

6093012	4/1994	Japan .
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20 Claims, No Drawings

SYNDIOTACTIC 1,2-POLYBUTADIENE SYNTHESIS

BACKGROUND OF THE INVENTION

Syndiotactic 1,2-polybutadiene (SPBD) is a thermoplastic resin which can be utilized in making films, fibers and molded articles. For example, U.S. Pat. No. 4,394,473 and U.S. Pat. No. 4,957,970 disclose the use of SPBD in making bags and packaging. It can also be blended into elastomers, such as polydiene rubbers. Because SPBD contains double bonds which are attached in an alternating fashion to its backbone, it can be cocured with the rubbers in such blends. In fact, SPBD/rubber blends provide a unique combination of properties which make them useful in various tire compounds.

U.S. Pat. No. 4,790,365 discloses that incorporation of SPBD into rubber compositions which are utilized in the supporting carcass or innerliner of tires greatly improves the green strength of those compositions. Electron beam precure (microwave precure) is a technique which has gained wide commercial acceptance as a means of improving the green strength of synthetic elastomers which are used in building tires. However, electron beam precure techniques are costly. The incorporation of SPBD into blends of such synthetic elastomers can often improve green strength to the degree that electron beam precure is not required. The incorporation of SPBD into halogenated butyl rubbers which are utilized as the innerliner compositions for tires also greatly improves the scorch safety of such compositions. U.S. Pat. No. 4,274,462 disclosed that pneumatic tires having improved resistance against heat build-up can be prepared by utilizing SPBD fibers in their tread base rubber.

According to U.S. Pat. No. 4,790,365, the SPBD utilized in making the supporting carcass for tires has a melting point which is within the range of 120° C. to 190° C. and that it is preferred for the SPBD utilized in making the supporting carcass to have a melting point which is within the range of 150° C. to 165° C. The SPBD utilized in making tire innerliners has a melting point which is within the range of 120° C. to 160° C. and preferably has a melting point which is within the range of 125° C. to 150° C. The melting points referred to herein are minimum endotherm values determined from DSC (differential scanning calorimetry) curves.

Techniques for preparing SPBD by polymerizing 1,3-butadiene monomer are well known in the art. These techniques include solution polymerization, suspension polymerization and emulsion polymerization. The SPBD made utilizing these techniques typically have a melting point within the range of about 195° C. to about 215° C. It is accordingly necessary to reduce the melting point of the SPBD to render it suitable for utilization in some applications.

A process is disclosed in U.S. Pat. No. 3,778,424 for the preparation of syndiotactic 1,2-polybutadiene which comprises polymerizing 1,3-butadiene in an organic solvent in the presence of a catalyst composition composed of:

- (a) a cobalt compound,
- (b) an organoaluminum compound of the formula AlR_3 , in which R is a hydrocarbon radical of 1-6 carbons and
- (c) carbon disulfide.

U.S. Pat. No. 3,901,868 reveals a process for producing a butadiene polymer consisting essentially of syndiotactic 1,2-polybutadiene by the successive steps of:

- (a) preparing a catalyst component solution by dissolving, in an inert organic solvent containing 1,3-butadiene, a

cobalt compound, soluble in the organic solvent, such as (i) cobalt- β -diketone complex, (ii) cobalt- β -keto acid ester complex, (iii) cobalt salt of organic carboxylic acid, and (iv) halogenated cobalt-ligand compound complex and an organoaluminum compound,

- (b) preparing a catalyst composition by mixing the catalyst component solution (prepared in step a) with an alcohol, ketone or aldehyde compound and carbon disulfide,

- (c) providing a polymerization mixture containing desired amounts of 1,3-butadiene, the catalyst composition and an inert organic solvent and

- (d) polymerizing 1,3-butadiene at a temperature which is within the range of -20° C. to 90° C.

U.S. Pat. No. 3,901,868 indicates that the melting point of the SPBD produced varies in response to the proportion of alcohol, ketone or aldehyde in the polymerization mixture. U.S. Pat. No. 4,153,767 shows that amide compounds, such as N,N-dimethylformamide, can be used in solution polymerizations to reduce the melting point of SPBD being synthesized.

U.S. Pat. No. 4,429,085 discloses a process for producing syndiotactic 1,2-polybutadiene by suspension polymerization in an aqueous medium. In this aqueous polymerization process, polybutadiene which has an essentially syndiotactic 1,2-microstructure is made by the steps of:

- (A) preparing a catalyst component solution by dissolving, in an inert organic solvent containing 1,3-butadiene (a) at least one cobalt compound selected from the group consisting of (i) β -diketone complexes of cobalt, (ii) β -keto acid ester complexes of cobalt, (iii) cobalt salts of organic carboxylic acids having 6 to 15 carbon atoms and (iv) complexes of halogenated cobalt compounds of the formula CoX_n , wherein X represents a halogen atom and n represents 2 or 3, with an organic compound selected from the group consisting of tertiary amine alcohols, tertiary phosphines, ketones and N,N-dialkylamides and (b) at least one organoaluminum compound of the formula AlR_3 , wherein R represents a hydrocarbon radical of 1 to 6 carbon atoms;
- (B) preparing a reaction mixture by mixing said catalyst component solution with a 1,3-butadiene/water mixture containing desired amounts of said 1,3-butadiene;
- (C) preparing a polymerization mixture by mixing carbon disulfide throughout said reaction mixture and
- (D) polymerizing said 1,3-butadiene in said polymerization mixture into polybutadiene while agitating said polymerization mixture.

U.S. Pat. No. 4,751,275 discloses a process for the preparation of SPBD by the solution polymerization of 1,3-butadiene in a hydrocarbon polymerization medium, such as benzene, toluene, cyclohexane or n-hexane. The catalyst system used in this solution polymerization contains a chromium-III compound which is soluble in hydrocarbons, a trialkylaluminum compound and a dialkylphosphite, such as di-neopentylphosphite or di-butylphosphite.

U.S. Pat. No. 4,902,741 and U.S. Pat. No. 5,021,381 discloses a process for preparing a syndiotactic 1,2-polybutadiene latex by emulsion polymerization which comprises polymerizing 1,3-butadiene monomer in an aqueous reaction mixture which is comprised of (1) water, (2) at least one emulsifier, (3) 1,3-butadiene monomer, (4) a catalyst emulsion composition which is prepared by dissolving in an inert organic solvent containing at least one polyene (a) at least one cobalt compound selected from the group consisting of (i) β -ketone complexes of cobalt, (ii) β -keto

acid ester complexes of cobalt, (iii) cobalt salts of organic carboxylic acids having 6 to 15 carbon atoms and (iv) complexes of halogenated cobalt compounds of the formula CoX_n , wherein X represents a halogen atom and n represents 2 or 3, with an organic compound selected from the group consisting of tertiary amine alcohols, tertiary phosphines, ketones and N,N-dialkylamides and (b) at least one organoaluminum compound of the formula AlR_3 wherein R represents a hydrocarbon radical of 1 to 6 carbon atoms to produce a catalyst component solution, and microfluidizing the catalyst component solution with an oil, a surfactant and water to an average particle size which is within the range of about 10 nanometers to about 1000 nanometers; and (5) at least one member selected from the group consisting of carbon disulfide and phenyl isothiocyanate.

The synthesis of SPBD in an aqueous medium offers several important advantages over solution polymerizations. Water, as a medium in which to carry out such a polymerization, is less expensive, more easily purified, less sensitive to oxygen and has a higher heat capacity. Conducting such polymerizations in an aqueous medium also permits for higher monomer and higher solids concentrations because of the lower viscosity of a polymer suspension or emulsion compared with that of a polymer solution. The main drawback associated with aqueous suspension and emulsion polymerizations for producing SPBD is the difficulty associated with reducing the melting point of the SPBD. In other words, it is difficult to control the chemical structure and hence the crystallinity and melting point of SPBD which is synthesized in an aqueous medium. Even though numerous modifiers can be used to reduce the level of crystallinity and resulting melting point of SPBD which is synthesized in solution, there are few efficient modifiers for reducing the crystallinity of SPBD which is synthesized in an aqueous medium.

U.S. Pat. No. 5,011,896 discloses the use of 4-(alkylamino)benzaldehydes, 4-(dialkylamino)benzaldehydes, 2,4-di-(alkoxy)benzaldehydes, 2,6-di-(alkoxy)benzaldehydes, 2,4,6-tri-(alkoxy)benzaldehydes and 4-(1-azacycloalkyl)benzaldehydes as modifiers for reducing the melting point of SPBD which is synthesized in an aqueous medium. U.S. Pat. No. 5,405,816 discloses the utilization of N,N-dibutylformamide as a highly effective modifier for reducing the melting point of SPBD synthesized in such polymerizations.

U.S. Pat. No. 5,468,822 discloses a 1,2-polybutadiene composition having an excellent reinforcing effect for rubber and synthetic resin materials which is comprised of at least two polybutadiene components having different melting points. Such compositions are synthesized by suspension-polymerizing 1,3-butadiene in a polymerization system containing water in the presence of a catalyst comprising at least one transition metal compound, at least one organic compound of the Group I to Group III metals and at least one member selected from the group consisting of carbon disulfide, phenyl isothiocyanate and xanthic acid, characterized in that, after the polymerization is started, a melting temperature-regulating agent comprising at least one member selected from the group consisting of ketones aldehydes, alcohols, esters, nitrites, sulfoxides, amides and phosphoric acid esters is added into the polymerization system in one adding operation or in two or more separate adding operations.

SUMMARY OF THE INVENTION

It has been unexpectedly found that SPBD having two distinct melting points can be synthesized in an aqueous

medium if the polymerization is conducted in the presence of a sodium halide salt or a potassium halide salt. By utilizing this polymerization technique, the process for making SPBD having at least two melting points can be greatly simplified. More specifically, the technique of this invention eliminates the need to add a melting point regulator to the polymerization medium after the polymerization is initiated.

Practicing the process of this invention can also lead to a more consistent polymer since it is not necessary to add melting point regulators at very specific points during the polymerization process. The possibility of failing to add the proper amount of melting point regulator and the necessary level of conversion to attain a desired polymer in commercial operations is also eliminated.

By conducting the polymerizations of this invention in the presence of a sodium halide salt or a potassium halide salt, the level of crystallinity is reduced in a portion of the SPBD synthesized. The melting point of the portion of the SPBD having reduced crystallinity is accordingly also reduced. The two melting points realized will correspond to the melting point of unmodified SPBD (about $190^\circ\text{C}.$ – $205^\circ\text{C}.$) and the melting point of SPBD made utilizing the melting point modifier in the absence of the sodium or potassium salt.

This invention more specifically discloses a process for preparing syndiotactic 1,2-polybutadiene having at least two different melting points which comprises polymerizing 1,3-butadiene monomer in an aqueous medium in the presence of a (1) catalyst system which is comprised of (a) transition metal compound, (b) an organoaluminum compound and (c) at least one member selected from the group consisting of carbon disulfide, phenyl isothiocyanate and xanthic acid, (2) at least one melting-point regulator and (3) a sodium halide salt or a potassium halide salt.

The subject invention also reveals a process for preparing syndiotactic 1,2-polybutadiene having at least two different melting points which comprises polymerizing 1,3-butadiene monomer in an aqueous medium in the presence of (1) a catalyst composition which is made by reacting (a) at least one cobalt compound selected from the group consisting of (i) β -diketone complexes of cobalt, (ii) β -keto acid ester complexes of cobalt, (iii) cobalt salts of organic carboxylic acids having 6 to 15 carbon atoms and (iv) complexes of halogenated cobalt compounds of the formula CoX_n , wherein X represents a halogen atom and n represents 2 or 3, with an organic compound selected from the group consisting of tertiary amine alcohols, tertiary phosphines, ketones and N,N-dialkylamides, (b) at least one organoaluminum compound of the formula AlR_3 , wherein R represents a hydrocarbon radical of 1 to 6 carbon atoms and (c) at least one conjugated diene; (2) at least one member selected from the group consisting of carbon disulfide, phenyl isothiocyanate and xanthic acid; (3) at least one melting-point regulator; and (4) a sodium halide salt or a potassium halide salt.

DETAILED DESCRIPTION OF THE INVENTION

The SPBD made in accordance with the techniques of this invention normally has more than about 70 percent of its monomeric units in a syndiotactic 1,2-configuration. In most cases, the SPBD made by the process of this invention will have from about 75 percent to about 95 percent of its monomeric units in a syndiotactic 1,2-configuration. The SPBD made by the process of this invention will also have at least two different melting points.

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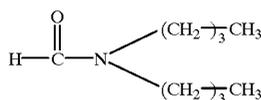
In practicing this invention, SPBD is synthesized utilizing aqueous suspension polymerization techniques or emulsion polymerization techniques. The catalyst system and general procedure needed for polymerizing 1,3-butadiene monomer into SPBD is described in U.S. Pat. No. 4,429,085. Such suspension polymerization techniques can be utilized in practicing this invention and the teachings of U.S. Pat. No. 4,429,085 are incorporated herein by reference in their entirety. A useful technique for preparing SPBD by emulsion polymerization is described in U.S. Pat. No. 4,902,741 and U.S. Pat. No. 5,021,381. The emulsion polymerization procedures described therein can be utilized in the practice of this invention and the teachings of U.S. Pat. No. 4,902,741 and U.S. Pat. No. 5,021,381 are accordingly incorporated herein by reference in their entirety.

In practicing this invention, 1,3-butadiene monomer is polymerized in an aqueous medium by suspension or emulsion polymerization techniques in the presence of a conventional melting-point regulator and a sodium or potassium halide salt. The melting point of SPBD is generally a reflection of the degree of crystallinity in the polymer. The higher the degree of crystallinity, the higher the melting point of the polymer. Thus, by reducing the level of crystallinity in a portion of the SPBD, an additional lower melting point results.

The melting-point regulators which can be utilized include ketones, aldehydes, alcohols, esters, nitriles, sulfonides, amides and phosphoric acid esters. In this aqueous polymerization process, there is a limitation of controlling crystallinity and melting point with agents which are water-soluble. Thus, ethanol and methanol are not as effective as other alcohols which are much less soluble in water than in hydrocarbons. In other words, water-soluble agents cannot be used as effectively to control crystallinity and melting point. A detailed description of the melting-point regulators which can be used to control crystallinity and melting points is given in U.S. Pat. No. 3,901,868, U.S. Pat. No. 4,153,767, U.S. Pat. No. 5,011,896 and U.S. Pat. No. 5,405,816. The teachings of these patents are incorporated herein by reference in their entirety.

As has been pointed out, water-soluble melting-point regulators, such as methanol and ethanol, are not effective agents. Other alcohols, such as 2-ethyl-1-hexanol, 1-decanol and 5-tridecanol which are not soluble in water, can be used with better success.

The N,N-dibutylformamide (DBF) is highly preferred for utilization as a melting-point modifier in practicing this invention. DBF has the structural formula:

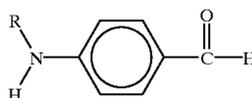


Lower N,N-dialkylformamides, such as N,N-dimethylformamide, N,N-diethylformamide and N,N-dipropylformamide, cannot be used as modifiers in such aqueous polymerizations because they hydrolyze in the aqueous polymerization mediums in which such suspension and emulsion polymerization are conducted. The use of higher N,N-dialkylformamides is not a commercially viable option because they are not very efficient and would need to be utilized in large quantities to attain a significant melting point reduction.

The aromatic aldehydes which can be utilized as modifiers in practicing this invention include

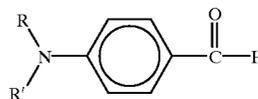
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- (a) 4-(alkylamino)benzaldehydes,
 (b) 4-(dialkylamino)benzaldehydes,
 (c) 2,4-di-(alkoxy)benzaldehydes,
 (d) 2,6-di-(alkoxy)benzaldehydes,
 (e) 2,4,6-tri-(alkoxy)benzaldehydes and
 (f) 4-(1-azacycloalkyl)benzaldehydes. The 4-(alkylamino)benzaldehydes which can be utilized as modifiers have the structural formula:



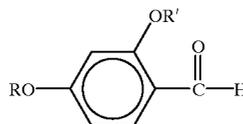
wherein R represents an alkyl group containing from about 1 to about 20 carbon atoms. It is preferred for such alkyl groups to contain from 4 to 8 carbon atoms.

The 4-(dialkylamino)benzaldehydes which can be utilized are of the structural formula:



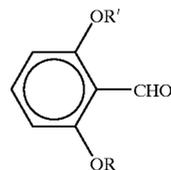
wherein R and R' can be the same or different and are alkyl groups which contain from 1 to 20 carbon atoms. It is preferred for R and R' to be alkyl groups which contain from 1 to about 8 carbon atoms.

The 2,4-di-(alkoxy)benzaldehydes which can be employed as modifiers have the structural formula:



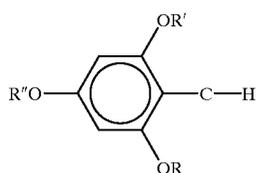
wherein R and R' can be the same or different and represent alkyl groups which contain from 1 to 20 carbon atoms. It is preferred for R and R' to represent alkyl groups which contain from 1 to 8 carbon atoms.

The 2,6-di-(alkoxy)benzaldehydes which can be utilized as modifiers in the practice of this invention are of the structural formula:



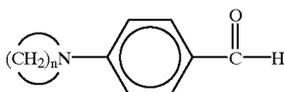
wherein R and R' can be the same or different and represent alkyl groups which contain from 1 to 20 carbon atoms. It is preferred for R and R' to represent alkyl groups which contain from 1 to 8 carbon atoms.

The 2,4,6-tri-(alkoxy)benzaldehydes which can be employed in the practice of this invention as modifiers have the structural formula:



wherein R, R' and R'' can be the same or different and represent alkyl groups containing from 1 to 20 carbon atoms. It is preferred for R, R' and R'' to represent alkyl groups which contain from 1 to 8 carbon atoms.

The 4-(1-azacycloalkyl)benzaldehydes that can be utilized as modifiers are of the general structural formula:



wherein n is an integer from 3 to about 8. It is preferred for n to be an integer from 4 to 6. In other words, it is preferred for the 4-(1-azacycloalkyl)benzaldehyde to be selected from the group consisting of

- 4-(1-azacyclobutyl)benzaldehyde,
- 4-(1-azacyclopentyl)benzaldehyde and
- 4-(1-azacyclohexyl)benzaldehyde.

In practicing this invention, standard suspension or emulsion polymerization techniques for synthesizing SPBD are carried out in the presence of at least one melting-point regulator and a sodium or potassium halide salt. The amount of melting-point regulator utilized will depend upon the desired lower melting point for the SPBD being prepared. Naturally, the utilization of larger quantities of the melting-point regulator will cause the lower melting point of the SPBD being synthesized to be at a lower temperature. Thus, if SPBD having a very low lower melting point is being sought, then a relatively large amount of the melting-point regulator will be utilized as a modifier in the polymerization. In cases where SPBD having a lower melting-point which is only slightly reduced is sought, a relatively low level of melting-point regulator will be needed.

As a general rule, the aqueous polymerization medium will contain from about 0.01 to about 2 phm (parts per hundred parts by weight of monomer) of the melting-point regulator. Usually from about 0.05 phm to about 1.25 phm of the melting-point regulator will be employed. In most cases where N,N-dibutylformamide is employed as the melting-point regulator, normally from about 0.1 phm to about 1.0 phm of the N,N-dibutylformamide will be utilized. To attain good conversions, less than about 0.5 phm and preferably less than about 0.25 phm of the N,N-dibutylformamide will be utilized. The table below shows the approximate relationship between conversion, melting point and the amount of N,N-dibutylformamide utilized as a melting-point regulator.

Amount of N,N-dibutylformamide	Monomer Conversion	SPBD Melting Point
0	99%	188° C.
0.25 phm	96%	120° C.
0.50 phm	85%	110° C.

-continued

	Amount of N,N-dibutylformamide	Monomer Conversion	SPBD Melting Point
5	1.00 phm	60%	105° C.
	1.25 phm	40%	104° C.

The sodium halide salt or the potassium halide salt employed in the aqueous polymerization medium will typically be a fluorine, chlorine, bromine or iodine salt. It is normally preferred for the halide to be fluorine, chlorine or bromine with chlorine salts being the most preferred. Some representative examples of salts which can be utilized include sodium fluoride, sodium chloride, sodium bromide, potassium fluoride, potassium chloride and potassium bromide. Potassium halide salts are normally greatly preferred since their utilization results two melting points which are more distinct. Thus, potassium bromide, potassium fluoride and potassium chloride are preferred salts with potassium chloride being the most preferred.

The sodium or potassium halide salt will normally be employed in the aqueous polymerization medium in an amount which is within the range of about 0.1 phr to about 20 phm. The sodium or potassium halide salt will typically be present in the aqueous polymerization medium in an amount which is within the range of 0.5 phm to 10 phm. It is normally preferred for the sodium halide salt or the potassium halide salt to be present in an amount which is within the range of 0.7 phm to about 5 phm with it being most preferred for the salt to be present in an amount which is within the range of 1 phr to 2 phm.

SUSPENSION POLYMERIZATION

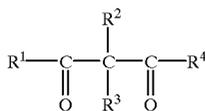
The first step in the synthesis of SPBD by suspension polymerization involves the preparation of a catalyst component solution. The catalyst component solution is prepared by dissolving at least one cobalt compound and at least one organoaluminum compound in an inert organic solvent containing at least one conjugated diene which is dissolved therein.

The term "an inert organic solvent" used herein refers to an organic solvent chemically inert to all of the catalyst components, the emulsifier, the 1,3-butadiene and the SPBD. Some representative examples of inert organic solvents include aromatic hydrocarbons, aliphatic hydrocarbons, alicyclic hydrocarbons, halogenated aromatic hydrocarbons and mixtures of two or more of the above-mentioned compounds. Some representative examples of aromatic hydrocarbons that can be utilized include benzene, toluene, xylenes, ethylbenzene, diethylbenzene or isobutylbenzene. The aliphatic hydrocarbons which can be used include n-hexane, isohexanes, n-heptane, n-octane, isooctanes, n-decane, 2,2-dimethylbutane, petroleum ether, kerosene, petroleum spirit or petroleum naphtha. The alicyclic hydrocarbons that can be used include cyclohexane and methylcyclohexane. Some representative examples of halogenated aromatic hydrocarbons that can be used include chlorobenzene, dichlorobenzenes or trichlorobenzenes.

The cobalt compound usable for the process of the present invention is soluble in an inert organic solvent selected from the group consisting of (i) β-diketone compounds, (ii) β-keto acid ester complexes of cobalt, (iii) cobalt salts of organic carboxylic acids having 1 to 25 carbon atoms and (iv) complexes of halogenated cobalt compounds of the formula CoX_n, wherein X represents a halogen atom and n represents 2 or 3, with an organic compound selected from the group

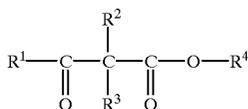
consisting of tertiary amines, alcohols, tertiary phosphines, ketones and N,N-dialkylamides.

The β -diketone compound which can be used to form a complex with a cobalt atom is of the formula:



wherein R^1 and R^4 , which are the same as or different from one another, are an alkyl radical of 1 to 6 carbon atoms and R^2 and R^3 , which are the same as or different from one another, are a hydrogen atom or an alkyl radical having 1 to 6 carbon atoms. This type of β -diketone complex of cobalt may be cobalt (ii) acetylacetonate or cobalt (iii) acetylacetonate.

The β -keto acid ester which can be used to form a complex with a cobalt atom may be of the formula:



wherein R^1 , R^2 , R^3 and R^4 are the same as defined above. This type of cobalt complex may be a cobalt-acetoacetic acid ethyl ester complex.

Some representative examples of cobalt salts of organic carboxylic acids that can be used include cobalt octoate and cobalt naphthanate.

The organoaluminum compound usable for the process of the present invention is of the formula AlR_3 wherein R represents a hydrocarbon radical containing from 1 to 6 carbon atoms. The hydrocarbon radical may be an alkyl radical or a cycloalkyl radical containing from about 1 to about 6 carbon atoms. The hydrocarbon radical may also be an aryl radical. Preferably, the organoaluminum compound will be trimethylaluminum, triethylaluminum triisobutylaluminum or triphenylaluminum.

In the preparation of the catalyst component solution, it is important that the cobalt compound and the organoaluminum compound are dissolved in the inert organic solvent containing at least one conjugated diene. Some conjugated dienes that can be used in making the catalyst component solution include 1,3-butadiene, 1,3-pentadiene, isoprene and myrcene. If the preparation is carried out in the absence of a conjugated diene, the resultant catalyst component solution is not effective as a component of the catalyst composition of the present invention. The conjugated diene is preferably used in a ratio by mole of at least 5, more preferably, within the range of 10 to 100, and most preferably within the range of 15 to 30, to the amount by mole of the cobalt compound to be used in the catalyst component solution. The preferred conjugated dienes for use in this invention are 1,3-butadiene and isoprene. The most preferred polyene is 1,3-butadiene.

The catalyst component solution is preferably prepared at a temperature of -25°C . to 50°C . and preferably contains 0.0005 to 1.0 moles per liter and more preferably 0.001 to 0.5 moles per liter of the cobalt compound. The temperature at which the catalyst component solution is prepared will more preferably be within the range of -10°C . to 10°C . and it is also highly desirable to use vigorous agitation in the preparation of the catalyst component solution. The ratio by

mole of the organoaluminum compound to the cobalt compound is preferably in a range from 0.2 to 50, more preferably, within the range of from 1 to 20, and most preferably within the range of 2 to 10.

In the preparation of the catalyst component solution, it is preferred for the cobalt compound to be first dissolved in the inert organic solvent in the presence of the polyene monomer and then for the organoaluminum compound to be added to the solution. However, very satisfactory results can also be obtained when the organoaluminum compound is added first.

In the preparation of this catalyst component solution, the organoaluminum compound should not be allowed to come in contact with water. This is because water can completely decompose such organoaluminum compounds. Accordingly, it is preferable that the inert organic solvent to be used to prepare the catalyst component solution be preliminarily dehydrated at least up to a content of water which is insufficient to completely decompose a significant amount of the organoaluminum compound.

It is preferable that the catalyst component solution be prepared using a dry (essentially water-free) inert organic solvent. However, a trace of water in the inert organic solvent can be present up to a concentration of about 500 ppm (parts per million by weight). It is preferred for no more than 50 ppm of water to be present in the inert organic solvent used in the preparation of the catalyst component solution. If a sufficient amount of water is present in the inert organic solvent used in the preparation of the catalyst component solution, the catalyst can be completely destroyed. The catalyst component solution will preferably be stored under an inert gas atmosphere, such as nitrogen, in the absence of sunlight or ultraviolet light.

It is desirable to allow the prereaction used in the preparation of the catalyst component solution to run for a period of at least 30 seconds, and more preferably for at least 1 minute before mixing the catalyst component solution with the oil, surfactant and water used in making the catalyst emulsion composition. Longer time periods can be used without the catalyst component solution losing its activity. In fact, the catalyst component solution can be stored for many weeks without losing activity if stored under an inert atmosphere.

After the organoaluminum compound has been incorporated in the catalyst component solution using the above-described technique, the catalyst becomes stable to water. This is presumably because of the formation of a π -allyl cobalt active specie. It is believed that it is this π -allyl bonding to the cobalt metal atom that imparts stability to this catalyst component, possibly by providing some hydrophobic shielding of the cobalt atom from water. Stability in polar solvents are well known for π -allyl complexes of other Group VIII transition metals of the periodic table to which cobalt belongs.

In the second step of the suspension polymerization procedure, a reaction mixture is prepared by mixing the catalyst component solution with a 1,3-butadiene/water mixture. The melting-point regulator and the sodium or potassium halide salt will also be added to the reaction mixture in the desired amount. A partitioning agent, such as gelatin, will normally be included in the reaction mixture to obtain a small polymer particle size. The amount of partitioning agent to be employed will preferably be within the range of about 0.75 to about 1.5 parts by weight per 100 parts by weight of 1,3-butadiene monomer to be polymerized. This 1,3-butadiene/water mixture can contain from as little as about 2 percent butadiene to as much as about 50 percent

butadiene by weight. It is preferred for this 1,3-butadiene/water mixture to contain from 15 percent to 35 percent by weight butadiene and it is more preferred for it to contain about 20 to 25 percent butadiene by weight. Since 1,3-butadiene is very volatile, it will be necessary to prepare this mixture in a closed system. Agitation will be provided in the preparation of the reaction mixture in order to insure formation of monomer droplets containing the catalyst component solution are distributed uniformly throughout the mixture. Since 1,3-butadiene is essentially insoluble in water, it will be present in this mixture in the form of droplets which are distributed throughout the mixture. If agitation is discontinued, there will be a separation of the organic and aqueous components of this mixture into two layers. The organic and aqueous layers of this reaction mixture can be mixed together again by agitating the reaction mixture.

In the third step of the suspension polymerization process, a polymerization mixture is prepared by adding carbon disulfide, phenyl isothiocyanate or xanthic acid to the above-described reaction mixture. It is normally preferred to utilize carbon disulfide. The molar ratio of carbon disulfide to 1,3-butadiene monomer will vary between about 1:600 and 1:2800. The molar ratio of carbon disulfide to monomer will preferably be within the range of about 1:1200 to about 1:1400. The molar ratio of monomer to cobalt will be within the range of 2500:1 to 10,000:1 and will preferably be within the range of 4500:1 to 5500:1.

In the final step of the suspension polymerization, the 1,3-butadiene monomer in the polymerization mixture is converted into polybutadiene while agitating the polymerization mixture. If the use of an antioxidant is desired, it may be added conveniently at the beginning of the polymerization. This polymerization of 1,3-butadiene monomer can be carried out at a temperature from about -20°C . to about 60°C . It is preferable for the polymerization temperature to be from -10°C . to 40°C . The most preferred polymerization temperature is about 0°C . to 10°C . At temperatures below 0°C ., an agent which will lower the freezing point of water can be added to the polymerization mixture to keep it from freezing.

This polymerization can be carried out either under a normal pressure or in a pressurized system. This polymerization can be carried out under a nitrogen atmosphere with good results. Such a polymerization can be run for a period of from about 1 to about 30 hours. It is generally preferred for the polymerization to be run for about 8 to about 10 hours. However, the optimum polymerization time will vary greatly with the polymerization temperature, catalyst, the amount of catalyst used, etc. The polybutadiene formed using the process of this invention will float to the surface of the polymerization mixture and can easily be recovered.

EMULSION POLYMERIZATION

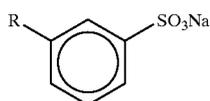
In cases where SPBD is made by emulsion polymerization, a catalyst component solution is made utilizing the same techniques that are employed in making catalyst component solutions for suspension polymerizations. Then, a catalyst emulsion composition is prepared by microfluidizing or microemulsifying the catalyst component solution with an oil, a surfactant and water. In preparing the catalyst emulsion composition, it is highly desirable to first mix the catalyst component solution with the oil and to separately mix the surfactant with the water. The catalyst component solution/oil mixture is then subsequently mixed with the surfactant/water mixture immediately prior to the microfluidization. The ratio of oil to catalyst component

solution will normally be within the range of about 0.5 to 30. It is normally preferred for the ratio of oil to catalyst component solution to be within the range of about 1 to about 10 and it is typically most preferred for the oil to catalyst component solution ratio to be within the range of about 2 to about 3. For example, a weight ratio of oil to catalyst component solution of about 2.5:1 is highly preferred.

The weight ratio of water to catalyst component solution utilized in preparing the catalyst emulsion composition is typically within the range of about 5 to about 80. It is normally preferred for the weight ratio of water to catalyst component solution to be within the range of about 10 to about 50. In most cases, it will be more preferred for the weight ratio of water to catalyst component solution utilized in preparing the catalyst emulsion composition to be within the range of about 20 to about 30. For instance, a weight ratio of water to catalyst component solution of about 27:1 is highly preferred for utilization in preparing the catalyst emulsion compositions of this invention. The weight ratio of surfactant to catalyst component solution utilized in preparing the catalyst emulsion composition will typically be within the range of about 0.001 to about 10. In most cases, it will be preferred to utilize a weight ratio of surfactant to catalyst component solution which is within the range of about 0.05 to 5. It is typically more preferred to utilize a ratio of surfactant to catalyst component solution which is within the range of about 0.1 to 0.3. Accordingly, a weight ratio of surfactant to catalyst component solution of about 0.2:1 is highly preferred.

The oil utilized in preparing the catalyst emulsion composition will typically be a long chain paraffinic oil. Such oils will generally be mixtures of various long chain hydrocarbons which contain from about 12 to about 28 carbon atoms. It is generally preferred for these compounds to be saturated. The oil will preferably be comprised of hydrocarbon compounds which contain from about 12 to about 18 carbon atoms. It is possible to utilize long chain alcohols which contain from about 12 to about 28 carbon atoms as the oil. However, it should be noted that such long chain alcohols can act as melting-point regulators. It is, accordingly, necessary to adjust the level of other melting-point regulators employed to attain the desired melting points for the SPBD in cases where long chain alcohols are employed as the oil. It is, of course, also possible to utilize a combination of paraffinic oils and alcohols to adjust the melting point of the SPBD as desired.

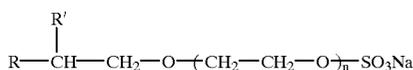
The surfactant utilized in preparing the catalyst emulsion composition will normally be an anionic surfactant or a nonionic surfactant. Some representative examples of types of anionic surfactants which can be utilized include carboxylates, alkylbenzene sulfonates, alkane sulfonates, α -olefin sulfonates, fatty alcohol sulfates and oxo-alcohol sulfates. Some representative examples of types of nonionic surfactants which can be utilized include alkylphenol ethoxylates, fatty-alcohol polyethyleneglycol ethers, oxo-alcohol polyethyleneglycol ethers, ethylene oxide polymers, propylene oxide polymers and fatty alcohol polyglycol ethers. It is generally preferred for the surfactant to be an anionic surfactant with alkyl benzene sulfonates, fatty alcohol sulfates and oxo-alcohol ether sulfates being most preferred. The alkyl benzene sulfonates which are utilized generally have the structural formula:



wherein R represents an alkyl group containing from 8 to 18 carbon atoms and preferably wherein R represents an alkyl group containing from 10 to 13 carbon atoms. The fatty alcohol sulfates which can be utilized normally have the structural formula:



wherein R represents an alkyl group containing from 6 to 28 carbon atoms and preferably wherein R represents an alkyl group containing from 11 to 17 carbon atoms. The oxo-alcohol ether sulfates which can be utilized generally have the structural formula:



wherein n is an integer from 1 to about 4 and wherein R and R' represent alkyl groups which can be the same or different with the total number of carbon atoms in R and R' ranging from about 11 to about 13.

The microfluidization procedure utilized results in the formation of a catalyst emulsion composition which has an average particle size which is within the range of about 10 to about 1,000 nanometers. The catalyst emulsion composition prepared will preferably have an average particle size which is within the range of about 30 to about 600 nanometers and will more preferably have an average particle size which is within the range of about 60 to about 300 nanometers. This microfluidization procedure can be carried out utilizing conventional microfluidizers or other equipment which is capable of homogenizing the catalyst emulsion composition to the desired particle size. For instance, the microfluidization can be carried out utilizing a high pressure pump or series of pumps. Ultrasonic and/or mechanical means can be utilized in the microfluidization procedure. To attain the desired particle size, it may be advantageous to pass the catalyst emulsion composition which is being prepared through the Microfluidizer™ more than one time.

The catalyst component solution utilized in preparing the catalyst emulsion composition is stable over long periods of time and can be stored for long periods without losing its activity. However, it is highly desirable to utilize the catalyst emulsion composition as soon as possible after it is prepared because the catalyst emulsion composition loses its activity over time. In practice, standard catalyst emulsion compositions lose essentially all of their activity after about 24 hours of being stored at room temperature. It is, accordingly, important to use the catalyst emulsion composition as soon as possible after its preparation. However, it is reported in U.S. Pat. No. 5,405,816 that the stability of the catalyst emulsion composition can be greatly improved if it is made with an amino acid soap. In fact, catalyst emulsion compositions which exhibit good activity for 24 hours can be made utilizing amino acid soaps. The amino acid soaps which can be utilized are generally salts of alkyl sarcosines. The alkyl groups in such alkyl sarcosines generally contain from about 8 to about 20 carbon atoms. These salts can be made by neutralization of the alkyl sarcosine with a base such as sodium, potassium, ammonium hydroxide,

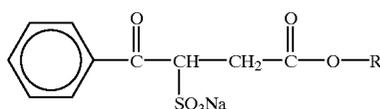
monoethanolamine, diethanolamine, triethanolamine or the like. Some representative examples of amino acid soaps which can be used include, sodium lauryl sarcosinate, sodium cocoyl sarcosinate, sodium myristoyl sarcosinate, sodium oleoyl sarcosinate and sodium stearoyl sarcosinate. In most cases, sodium lauroyl sarcosinate will be used as the amino acid soap.

The aqueous reaction mixture is prepared by mixing (1) water, (2) at least one emulsifier, (3) 1,3-butadiene monomer, (4) the catalyst emulsion composition, (5) carbon disulfide, phenyl isothiocyanate and/or xanthic acid, (6) the melting-point regulator and (7) the potassium halide salt or the sodium halide salt. Water is the major component in the aqueous reaction mixture. The amount of 1,3-butadiene monomer in the aqueous reaction mixture will vary from about 2 weight percent to about 50 weight percent. However, in most cases, it will be preferred for the aqueous reaction mixture to contain from about 10 weight percent to about 40 weight percent 1,3-butadiene monomer. It will generally be more preferred for the aqueous reaction mixture to contain from about 20 to about 30 weight percent 1,3-butadiene monomer. The amount of emulsifier utilized in preparing the aqueous reaction mixture will normally be within the range of about 0.1 phm to about 10 phm (parts per hundred parts of monomer). It will normally be preferred for the emulsifier to be present in an amount ranging from about 0.5 phm to about 5 phm. In most cases, it will be more preferred for the emulsifier to be present in an amount within the range of about 1 phm to about 3 phm.

The emulsifiers used in the emulsion polymerization of 1,3-butadiene into SPBD may be charged at the outset of the polymerization or may be added incrementally or by proportioning as the reaction proceeds. Generally, anionic emulsifier systems provide good results; however, any of the general types of anionic, cationic or nonionic emulsifiers may be employed in the polymerization.

Among the anionic emulsifiers that can be employed in such emulsion polymerizations are fatty acids and their alkali metal soaps such as caprylic acid, capric acid, pelargonic acid, lauric acid, undecylic acid, myristic acid, palmitic acid, margaric acid, stearic acid, arachidic acid and the like; amine soaps of fatty acids such as those formed from ammonia, mono- and dialkyl amines, substituted hydrazines, guanidine and various low molecular weight diamines; chain-substituted derivatives of fatty acids such as those having alkyl substituents; naphthenic acids and their soaps and the like; sulfuric esters and their salts, such as the tallow alcohol sulfates, coconut alcohol sulfates, fatty alcohol sulfates, such as oleyl sulfate, sodium lauryl sulfate and the like; sterol sulfates; sulfates of alkylcyclohexanols, sulfation products of lower polymers of ethylene as C10 to C20 straight chain olefins, and other hydrocarbon mixtures, sulfuric esters of aliphatic and aromatic alcohols having intermediate linkages, such as ether, ester or amide groups such as alkylbenzyl (polyethyleneoxy) alcohols, the sodium salt of tridecyl ether sulfate; alkane sulfonates, esters and salts, such as alkylchlorosulfonates with the general formula RSO_2Cl , wherein R is an alkyl group having from 1 to 20 carbon atoms, and alkylsulfonates with the general formula $\text{RSO}_2\text{—OH}$, wherein R is an alkyl group having from 1 to 20 carbon atoms; sulfonates with intermediate linkages such as ester and ester-linked sulfonates such as those having the formula $\text{RCOOC}_2\text{H}_4\text{SO}_3\text{H}$ and $\text{ROOC—CH}_2\text{—SO}_3\text{H}$, wherein R is an alkyl group having from 1 to 20 carbon atoms such as dialkyl sulfosuccinates; ester salts with the general formula:

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wherein R is an alkyl group having from 1 to 20 carbon atoms; alkylaryl sulfonates in which the alkyl groups contain preferably from 10 to 20 carbon atoms, e.g. dodecylbenzenesulfonates, such as sodium dodecylbenzene sulfonate; alkyl phenol sulfonates; sulfonic acids and their salts such as acids with the formula RSO_3Na , wherein R is an alkyl and the like; sulfonamides; sulfamido methylene-sulfonic acids; rosin acids and their soaps; sulfonated derivatives of rosin and rosin oil; and lignin sulfonates, and the like.

Carboxylate emulsifiers are highly preferred. This is because their utilization leads to less build-up on the walls of the polymerization reactor. Fatty acid soaps and rosin acid soaps are representative examples of highly preferred carboxylate soaps. Of rosin acids, about 90 percent are isomeric with abietic acid and the other 10 percent is a mixture of dehydro abietic acid and dihydro abietic acid.

Agitation should be provided in the preparation of the aqueous reaction mixture to ensure that the catalyst emulsion composition, the monomer and the surfactant are distributed essentially homogeneously throughout the mixture. Since 1,3-butadiene monomer is very volatile, it will be necessary to prepare the aqueous reaction mixture under pressure in a closed system.

The carbon disulfide, phenyl isothiocyanate or xanthic acid is typically the last component to be added to the aqueous reaction mixture. The addition of the carbon disulfide, phenyl isothiocyanate or the xanthic acid to the reaction mixture which already contains the catalyst emulsion composition will initiate the polymerization reaction. It is normally preferred to utilize carbon disulfide. The amount of carbon disulfide that can be added will vary between 0.005 phm and 2 phm. More preferably, the amount of carbon disulfide added will vary between 0.001 and 1 phm.

In the process of the present invention, the larger the proportion of the carbon disulfide in a range from about 0.0005 phm to about 0.5 phm in the polymerization mixture, the larger the yield of the SPBD obtained from the polymerization mixture. However, too large an amount of carbon disulfide, for example, larger than about 0.5 phm, causes a decrease in the polymer yield.

The 1,3-butadiene monomer is polymerized into SPBD while agitating the polymerization mixture. If the use of an antioxidant is desired, it may be added conveniently at the beginning of the polymerization. This polymerization of 1,3-butadiene monomer can be carried out at a temperature from about -20°C . to about 90°C . It is preferable for the polymerization temperature to be from -10°C . to 40°C . The most preferred polymerization temperature is about 0°C . to about 10°C . At temperatures below 0°C ., an antifreeze agent can be added to the polymerization mixture to keep it from freezing.

This polymerization can be carried out either under a normal pressure or in a pressurized system. This polymerization can be carried out under an inert gas atmosphere, such as a nitrogen atmosphere, with good results. Such a polymerization can be run for a period of from about 3 to about 30 hours. It is generally preferred for the polymerization to be run for a period which is within the range of about 10 to 16 hours. However, the optimum polymerization time will vary greatly with the polymerization temperature,

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catalyst, the amount of catalyst used, etc. In most cases, the optimum polymerization time will be within the range of about 12 to about 14 hours.

After the polymerization has been completed, the SPBD can be recovered from the latex by standard coagulation techniques. For instance, coagulation can be accomplished by adding acids or blends of salts with acids to the latex. For example, sulfuric acid, hydrochloric acid, blends of sodium chloride with sulfuric acid and blends of hydrochloric acid with methanol are very effective as coagulating agents. Calcium chloride solutions and blends of calcium chloride with various acids can also be utilized as coagulants. Salt/acid coagulants are generally preferred. For instance, the utilization of sulfuric acid with sodium chloride or potassium chloride as the coagulant will lead to good results. Barium chloride and magnesium sulfate are additional examples of divalent salts which are suitable for utilization in coagulating the SPBD latex. It may also be advantageous to employ materials classified as coagulation aids, such as high molecular weight polyelectrolytes, in the coagulation of the SPBD latex. The preferred coagulation aids are weak bases. Some representative examples of suitable coagulation aids which can be used include Nalco™ 108 (Nalco Chemical Company), Daxad™ CP-1 (W. R. Grace and Company), and similar materials that are also weakly basic polyelectrolytes. The quantity of coagulant required will vary with the emulsifier, the amount of emulsifier used, the rubber being coagulated and the type of coagulant being employed. Generally, the optimum type of coagulant, quantity of coagulant and coagulating conditions can be determined using a trial-and-error approach.

The following working examples illustrate various embodiments of the process of the present invention. These examples are intended merely to illustrate the present invention and not in any sense to limit the scope in which the present invention can be practiced. Unless specifically indicated otherwise, parts and percentages are given by weight.

EXAMPLE 1

In this experiment, a SPBD having two distinct melting points was synthesized in an aqueous medium in the presence of potassium chloride utilizing the technique of this invention. In the procedure used, an antioxidant solution was prepared by mixing 17 grams of Irganox antioxidant, 6.8 of 2,2'-methylene bis(4-methyl-6-tertiarybutyl phenol), 6.8 grams of 2,5-di-t-pentylhydroquinone, 6.8 grams of ammonium lauroyl sarcosinate solution and 510 grams of water. A suspension solution was made by mixing 10,812 grams of water, 75.48 grams of polyacrylic copolymer, 51 grams of potassium chloride and 10 grams of potassium hydroxide. A catalyst solution was made by mixing 13.44 grams of triisobutylaluminum, 3.36 grams of cobalt octanoate, 7.47 grams of 1,3-butadiene and 102.82 grams of hexane. An activator solution was made by mixing 1.28 grams of carbon disulfide and 1788.4 grams of water. Finally, a monomer solution was made by mixing 680 grams of hexane, 8.16 grams of N,N-dibutylformamide and 1859.8 grams of 1,3-butadiene.

The antioxidant solution, 40 percent of the suspension solution and 40 percent of the activator solution were initially charged into a reactor which was maintained at a temperature of 50°F . (10°C .) and agitated. Then, the remaining suspension solution, the remaining activator solution, the catalyst solution and the monomer solution were continuously fed into the reactor over a period of 2 hours. The suspension solution was fed into the reactor at a flow rate of 54.44 grams per minute, the catalyst solution

was fed at a flow rate of 1.06 grams per minute, the activator solution was fed at a flow rate of 8.96 grams per minute and the monomer solution was fed at a flow rate of 21.23 grams per minute.

The SPBD made by this aqueous polymerization technique was determined to have two distinct melting points. The first melting point was observed at a temperature of about 145° C. and the second melting point was observed at a temperature of about 195° C. This experiment accordingly shows that the technique of this invention can be utilized to synthesize SPBD having two different melting-points.

EXAMPLE 2

The procedure utilized in Example 1 was repeated in this experiment except the potassium chloride used in Example 1 was replaced with sodium chloride. The SPBD made by this aqueous polymerization technique was again determined to have two distinct melting points. The first melting point was observed at a temperature of about 145° C. and the second melting point was observed at a temperature of about 195° C. However, the melting point observed at 195° C. was not as distinct as the melting point observed at 195° C. in Example 1. This experiment accordingly shows that sodium chloride can be utilized to synthesize SPBD having two different melting-points.

COMPARATIVE EXAMPLE 3

The procedure utilized in Example 1 was repeated in this experiment except that potassium chloride was not added to the suspension solution. The SPBD made by this aqueous polymerization technique had only one melting point at a temperature of about 140° C. This experiment accordingly shows that a sodium or potassium salt is required to produce SPBD having two different melting-points.

While certain representative embodiments and details have been shown for the purpose of illustrating the subject invention, it will be apparent to those skilled in this art that various changes and modifications can be made therein without departing from the scope of this invention.

What is claimed is:

1. A process for preparing syndiotactic 1,2-polybutadiene having at least two different melting points which comprises polymerizing 1,3-butadiene monomer in an aqueous medium in the presence of a (1) catalyst system which is comprised of (a) transition metal compound, (b) an organoaluminum compound and (c) at least one member selected from the group consisting of carbon disulfide, phenyl isothiocyanate and xanthic acid, (2) at least one melting-point regulator and (3) a salt selected from the group consisting of sodium halide salts and potassium halide salts.

2. A process as specified in claim 1 wherein the salt is selected from the group consisting of sodium fluoride, sodium chloride, sodium bromide, potassium fluoride, potassium chloride and potassium bromide.

3. A process as specified in claim 2 wherein the salt is present in an amount which is within the range of about 0.1 phr to about 20 phr.

4. A process as specified in claim 3 wherein the melting-point regulator is an alcohol.

5. A process as specified in claim 3 wherein said polymerization is a suspension polymerization.

6. A process as specified in claim 5 wherein the melting-point regulator is N,N-dibutylformamide.

7. A process as specified in claim 5 wherein the salt is selected from the group consisting of potassium fluoride, potassium chloride and potassium bromide.

8. A process as specified in claim 7 wherein the salt is present in an amount which is within the range of 0.5 phr to about 10 phr.

9. A process as specified in claim 8 wherein the salt is potassium chloride.

10. A process as specified in claim 9 wherein the salt is present in an amount which is within the range of 0.7 phr to 5 phr.

11. A process as specified in claim 9 wherein the salt is present in an amount which is within the range of 1 phr to 2 phr.

12. A process for preparing syndiotactic 1,2-polybutadiene having at least two different melting points which comprises polymerizing 1,3-butadiene monomer in an aqueous medium in the presence of (1) a catalyst composition which is made by reacting (a) at least one cobalt compound selected from the group consisting of (i) β -diketone complexes of cobalt, (ii) β -keto acid ester complexes of cobalt, (iii) cobalt salts of organic carboxylic acids having 6 to 15 carbon atoms and (iv) complexes of halogenated cobalt compounds of the formula CoX_n , wherein X represents a halogen atom and n represents 2 or 3, with an organic compound selected from the group consisting of tertiary amine alcohols, tertiary phosphines, ketones and N,N-dialkylamides, (b) at least one organoaluminum compound of the formula AlR_3 , wherein R represents a hydrocarbon radical of 1 to 6 carbon atoms and (c) at least one conjugated diene; (2) at least one member selected from the group consisting of carbon disulfide, phenyl isothiocyanate and xanthic acid; (3) at least one melting-point regulator; and (4) at least one salt selected from the group consisting of sodium halide salts and potassium halide salts.

13. A process as specified in claim 12 wherein the salt is selected from the group consisting of sodium fluoride, sodium chloride, sodium bromide, potassium fluoride, potassium chloride and potassium bromide; and wherein the salt is present in an amount which is within the range of about 0.1 phr to about 20 phr.

14. A process as specified in claim 13 wherein the melting-point regulator is selected from the group consisting of ketones, aldehydes, alcohols, esters, nitriles, sulfoxides, amides and phosphoric acid esters.

15. A process as specified in claim 14 wherein said cobalt compound is a cobalt salt of an organic carboxylic acid containing from 6 to 15 carbon atoms.

16. A process as specified in claim 15 wherein said polymerization is a suspension polymerization.

17. A process as specified in claim 16 wherein said member selected from the group consisting of carbon disulfide, phenyl isothiocyanate and xanthic acid is carbon disulfide.

18. A process as specified in claim 17 wherein said polymerization is conducted at a temperature which is within the range of about -10° C. to about 40° C.

19. A process as specified in claim 18 wherein the melting-point regulator is N,N-dibutylformamide; wherein the salt is selected from the group consisting of potassium fluoride, potassium chloride and potassium bromide; and wherein the salt is present in an amount which is within the range of 0.5 phr to about 10 phr.

20. A process as specified in claim 19 wherein the salt is potassium chloride; and wherein the potassium chloride salt is present in an amount which is within the range of 0.7 phr to 5 phr.